



Pyrolysis characteristics and kinetic analysis of different dewatered sludge



Qiang Zhang, Huan Liu, Peng Liu, Hongyun Hu, Hong Yao^{*}

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

HIGHLIGHTS

- The pyrolysis characteristics of different sludge were analyzed by using TG-FTIR.
- Raw sludge mainly decomposed at 378–676 K.
- The decomposition temperature of conditioned sludge was prolonged to 823 K.
- The main gaseous products were NH₃, CH₄, CO and CO₂.
- Global reaction model can describe both dry and wet sludge pyrolysis reaction.

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ABSTRACT

Pyrolysis behavior and kinetic properties of four different sludge, including raw sludge and three sludge respectively dewatered with FeCl₃/CaO, FeCl₃/CaO/coal and Fenton's reagent (Fe²⁺ + H₂O₂)/CaO, were analyzed by using thermogravimetry coupled with Fourier transform infrared spectrometry (TG-FTIR). The results show that organics of raw sludge mainly decomposed at 378–676 K, and the decomposition temperature of conditioned sludge was prolonged to 823 K. Addition of coal and catalysis of CaO/ferric salt both promoted sludge pyrolysis, leading to more NH₃, CH₄ and CO productions. Compared with dry sludge, wet sludge pyrolysis was hard to finish completely, and the first peak of organics' decomposition appeared at higher temperature (about 573 K). Additionally, the global reaction model was suited to determine kinetic parameters, which showed that dry sludge conditioned with more CaO addition had higher *E* values than those of dry raw sludge. Opposite results were obtained when sludge samples were wet.

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1. Introduction

Sludge contains highly complex organics, such as proteins, cellulose, hemi-cellulose and lignin, which can be regarded as a special source of bioenergy (Parnaudeau and Dignac, 2007). Similar to biomass thermal utilization, pyrolysis is also an effective sludge disposal method for energy recovery, and high-added value products such as tar and fuel gas can be generated (Dominguez et al., 2006a,b). However, the large amounts of moisture in raw sludge (97–99%) or in traditional dewatered sludge (80–85%) will consume a high amount of energy during thermal disposal of sludge (Liu et al., 2013). Although direct pyrolysis of wet sludge has been proved to be in favor of fuel gas generation (Dominguez et al., 2006a,b; Liu et al., 2014), the yields scarcely increase when the

water content reaches a certain extent (about 47%) (Xiong et al., 2013). Therefore, it is necessary to control moisture at a lower level (less than 60%).

In recent years, chemical conditioners such as Fe(II)-activated persulfate, coal ashes, H₂O₂ and CaO are added to enhance sludge dewaterability, which successfully reduces water content of sludge to 50–60% (Zhen et al., 2012; Thapa and Hoadley, 2009; Liu et al., 2013; Zhai et al., 2012). Nevertheless, sludge pyrolysis characteristic may be changed with adding conditioners. According to the literature, iron salt can catalyze tar breakdown and consequently increase syngas production (Nordgreen et al., 2006). Calcium compounds can improve combustible gas quality and lower reaction temperature by catalyzing or absorbing CO₂ (Sirimirin et al., 2013; Chiang et al., 2011). Moreover, the harmful gases, for example NH₃, also can be effected by mineral matter (Ren et al., 2013), which will influence the quality of fuel gases. However, inorganic compounds in those studies are mostly added through physical

^{*} Corresponding author. Tel./fax: +86 27 87545526 (O).

E-mail address: hyao@hust.edu.cn (H. Yao).

mixing, not as chemical conditioners. Our previous work showed that the conditioners of dewatered sludge provide different performance on sludge gasification (Liu et al., 2013).

Several researchers studied the pyrolysis characteristics of fuels through TG-FTIR (GaO et al., 2014; Ren et al., 2009). Through these methods, not only the gas releasing from pyrolysis can be observed, but also the kinetic parameters can be received by TG curves, which can provide deeper insights into the mechanism of pyrolysis. Several models have been built to predict the sludge pyrolysis mechanism for fuel production (Yang and Jiang, 2009; Manara and Zabaniotou, 2012). Among these, the global reaction model is suitable to describe biomass pyrolysis within narrow temperature ranges and has an effective activation energy and pre-exponential factor, which are suited to pyrolysis of both raw sludge and sludge conditioned with FeCl₃ and CaO (Allan et al., 2013; Folgueras et al., 2010, 2013). Some mineral matter also can change pyrolysis kinetic parameters of materials (Vamvuka et al., 2006). Therefore, it is of necessity to understand the effect of conditioners on performance and kinetics of sludge pyrolysis.

In this study, pyrolysis characteristics of the wet and dry sludge were analyzed using TG-FTIR. The influence of conditioners (FeCl₃/CaO, FeCl₃/CaO/coal, Fenton's reagent (Fe²⁺+H₂O₂)/CaO), and moisture can be generated through the information of devolatilization curves and gaseous species evolution (NH₃, CH₄, CO and CO₂). In order to further compare different sludge pyrolysis characteristics, kinetic parameters were determined by using global reaction model in each organics reaction stage.

2. Methodology

2.1. Materials

The raw sludge (RS) was collected from a municipal wastewater treatment plant in Wuhan, China, and the water content was 69.45%. Then the RS was conditioned with FeCl₃/CaO (named as Fe–Ca sludge), FeCl₃/CaO/coal (named as Fe–Ca–C sludge), Fenton's reagent (Fe²⁺+H₂O₂)/CaO (named as Fenton–Ca sludge), respectively. The details of conditioning and dewatering process are shown in a previous work (Liu et al., 2012). It should be noticed that the amount of CaO added in Fe–CaO–C sludge accounts for a fifth of that in Fe–CaO and Fenton–CaO sludge. After filter press dewatering the corresponding water contents were 43.48%, 45.38% and 34.32%, respectively. These sludges were separately subjected to drying (378 K for 24 h), crushing, and screening. Table 1 reports the proximate and ultimate analysis of four sludge samples, as well as a bituminous coal used in this work.

2.2. TG-FTIR analysis

Non-isothermal pyrolysis of wet and dry sludge was carried out online by a TGA type (NETZSCH, STA 409, Germany) coupled with a FTIR type (BRUKER, EQUINOX 55, Germany). About 78.5–82.5 mg

samples were heated from 303 to 1373 K at 40 K/min under pure nitrogen of 100 mL/min. The volatiles released were monitored by FTIR with spectrum ranging from 4000 to 400 cm^{−1}.

2.3. Kinetic parameters of different sludge

The global reaction was considered in each stage of decomposition of organics. The pyrolysis reaction equation can be simple described as Eqs. (1) and (2) (Thipkhunthod et al., 2006):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where α is the reaction conversion which is obtained by Eq. (3), t is the time, T is the temperature, $f(\alpha)$ is the mechanism function, A is the pre-exponential factor, E is the activation energy and R is the gas constant.

$$\alpha = \frac{W_o - W}{W_o - W_\infty} \quad (3)$$

where W_o , W and W_∞ are the initial mass, mass at time t and final mass of sample, respectively. To the non-isothermal pyrolysis, the heating rate β is a constant:

$$\beta = \frac{dT}{dt} \quad (4)$$

Eq. (5) is the integration of the Eqs. (1), (2) and (4):

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = -\left(\frac{E}{RT}\right) + \ln\left(\frac{AR}{\beta E}\right) \quad (5)$$

According to the Eq. (5), when an appropriate functional expression was chosen, a line could be drawn by $\ln\left(\frac{G(\alpha)}{T^2}\right) - \frac{1}{T}$ and kinetic parameters A and E could be determined by slope and intercept.

Sludge is similar to biomass, so n th-order chemical reaction function was taken as mechanism function. Eqs. (6) and (7) are the $f(\alpha)$ and $G(\alpha)$. The best n value was chosen for the height correlation coefficient R^2 value.

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

$$G(\alpha) = [(1 - \alpha)^{-(n-1)} - 1]/(n - 1) \quad (7)$$

3. Results and discussion

3.1. TGA analysis of different dewatered sludge

Fig. 1 shows the TG and DTG curves of different wet and dry sludge. The final weight losses of dry sludge were 61.05% (RS), 59.16% (Fe–CaO sludge), 58.18% (Fe–CaO–C sludge) and 71.47% (Fenton–CaO sludge), while those for the corresponding wet ones were 78.00%, 64.09%, 65.89% and 56.89%. For the wet sludge, the main weight loss was attributed to the water evaporation. The real

Table 1
Proximate and ultimate analysis of bituminous coal and four sludge samples.

Materials	Proximate analysis (wt%) ^a				Ultimate analysis (wt%) ^a				
	M	V	A	FC	C	H	N	S	O ^b
Bituminous coal	4.30	37.18	14.43	44.09	56.61	5.42	0.82	1.72	16.70
Raw sludge	1.63	55.84	39.25	3.28	30.21	4.64	5.90	0.91	17.46
Fe–CaO sludge	3.75	42.65	53.19	0.41	19.08	3.80	3.38	0.11	16.69
Fe–CaO–C sludge	4.47	49.27	37.79	8.47	34.99	4.30	3.94	0.94	13.57
Fenton–CaO sludge	3.06	40.94	55.20	0.80	18.61	3.42	3.22	0.51	15.98

^a Dry ash basis.

^b Calculated by difference.

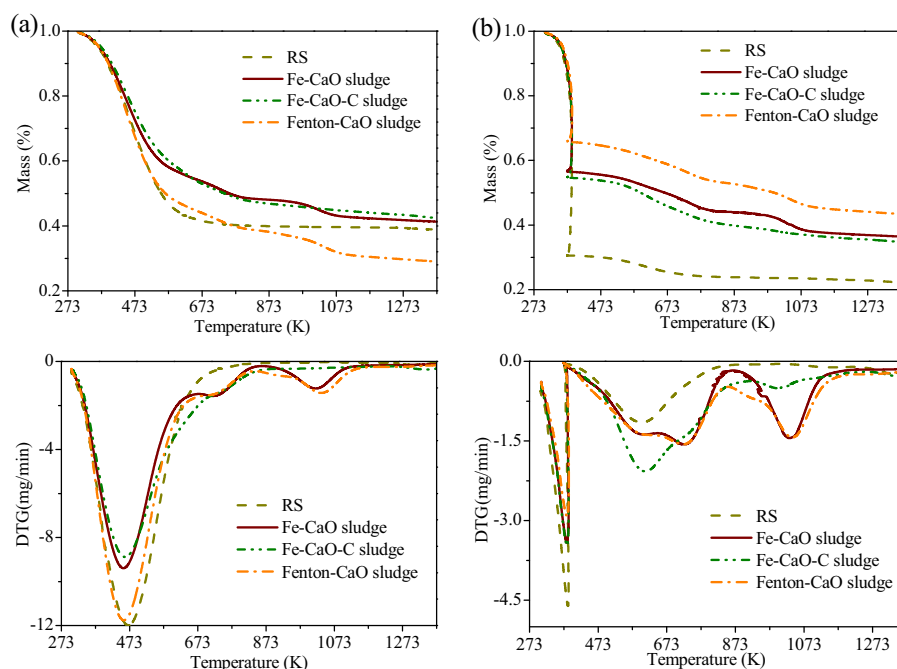


Fig. 1. TG and DTG curves of different sludge pyrolysis: (a) dry sludge and (b) wet sludge.

decomposed organics account for 27.99%, 36.46%, 37.55% and 34.36% (dry basis of sludge), which are much less than the pyrolysis of dry sludge. From this observation we concluded that the pyrolysis of wet sludge hardly occurs completely at a low heating rate (40 K/min).

Table 2 shows the pyrolysis information from DTG curves. It is clear that organics' decomposition primarily occurs below 800 K. Only a single devolatilization peak appeared in both dry RS and Fe-Ca-C sludge pyrolysis. However for the latter the peak was broader and bigger especially at 598–800 K, which might be associated with coal pyrolysis. In addition, both dry Fe-Ca and Fenton-Ca sludge consisted of a peak and a shoulder at 378–600 K and 700–780 K, also a remarkable peak due to CaCO_3 decomposition at 873–1073 K. As for wet sludge pyrolysis, an obvious sharp peak was observed, indicating the fast rate of water desorption. Considering that evaporation is endothermic, the actual sample temperature kept lower, resulting in a delay of 130–150 K for the initial devolatilization of wet sludge. Although wet Fe-CaO and Fenton-CaO sludge also exhibited two intervals for organics' decomposition, the second peak was bigger than the first one, which was different from dry ones. In general, the weight loss was less on each stage for wet sludge.

Since moisture mainly affected the first peak of organics' decomposition, FTIR spectrums of this point from different sludge were further detected. The results showed that all sludge contained the

similar gas production, H_2O ($4000\text{--}3600\text{ cm}^{-1}$), CH_4 ($3100\text{--}2800\text{ cm}^{-1}$), CO_2 ($2400\text{--}2250\text{ cm}^{-1}$), CO ($2250\text{--}2000\text{ cm}^{-1}$) and NH_3 ($1000\text{--}850\text{ cm}^{-1}$). But there was an exception for dry Fenton-CaO sludge, of which the main spectrums were at $1900\text{--}1200\text{ cm}^{-1}$. That may be the emission of small molecule lipid, aldehydes and acids. Yang et al. (2012) considered that the absorption bonds at 1700 cm^{-1} and 1740 cm^{-1} may be R-CHO and R-CO-R' caused by disintegration of hemicelluloses and lignin. Furthermore, the similar wavenumber was regarded as acids by other researchers (Han et al., 2010). The difference may be connected with high volatile fatty acids concentration caused by strong Fenton oxidation (Michalska et al., 2012). But different results were obtained for wet Fenton-CaO sludge. The first organics' decomposition peak appeared at 461 K for the dry one and 608 K for the wet one (see Table 2). Perhaps because of higher reaction temperature, CO_2 and CH_4 were the main gas products at first peak from the wet one.

3.2. NH_3 release characteristics

As mentioned above, NH_3 is also the main gas production from sludge pyrolysis. As listed in Table 1, the N content of sludge was high. During the pyrolysis process, nitrogen in sludge was released in the forms of NH_3 and HCN from labile proteins or amine-N

Table 2
Temperature and weight loss (dry basis) of organics decomposition peaks in different sludge pyrolysis.

Materials		First organics peak		Second organics peak	
		$T(\text{peak})/\text{K}$	WL/%	$T(\text{peak})/\text{K}$	WL/%
Dry sludge	RS	378–676(474)	52.4		
	Fe-CaO	378–600(460)	36.7	716–780(721)	2.7
	Fe-CaO-C	378–800(465)	46.3		
	Fenton-CaO	378–600(461)	45.8	700–780(720)	3.2
Wet sludge	RS	500–700(605)	15.4		
	Fe-CaO	530–646(612)	6.7	646–800(730)	11.0
	Fe-CaO-C	520–780(615)	20.7		
	Fenton-CaO	500–620(608)	5.2	620–800(726)	10.5

compounds decomposition (Zhang et al., 2013; Tian et al., 2013). Fig. 2 shows the NH_3 release curves of different sludge pyrolysis.

Although the RS had the highest N content, the emission of NH_3 was the minimum of all. Furthermore, the release time was earlier in the case of conditioned dry and wet sludge (except for dry Fenton–CaO sludge). In previous research, conditioned sludge had a high pH (about 11.7), more than that of RS (6.8) (Liu et al., 2012). Therefore, the alkaline solution is easy for ammonium dissolution, and some NH_3 or NH_4^+ may be absorbed on the particle surface during drying. Tian et al. (2002) also observed NH_3 at low temperature, suspecting that NH_3 is generated from the ammonium salts in sludge. However for dry Fenton–Ca sludge, the NH_3 did not release until 300 s (about 473 K). Our previous study (Liu et al., 2012) found that a large amount of NH_3 had released during the conditioning process for this type of sludge. The other possible reason is that $\text{NH}_3/\text{NH}_4^+$ had been convert to other stable oxidized N-containing compounds after strong Fenton oxidation.

Besides, there existed a second peak of NH_3 emission for dry Fe–Ca and Fenton–Ca sludge pyrolysis, owing to the addition of more CaO. As a catalyst, CaO has a good potential to catalyze organics' decomposition and tar cracking. Jeremias et al. (2014) suggested that the dolomitic limestone improved the fuel-N conversion into NH_3 via char conversion. Ren et al. (2013) demonstrated that iron and calcium compounds had a strong positive catalytic effect on NH_3 formation from aspartic acid. Also due to the strong Fenton oxidation, some bacteria or macromolecule non-biodegradable organics had been possibly converted into smaller protein and amino acids during dewatering, which may decompose easily at low temperature, leading to more NH_3 yields from Fenton–Ca sludge than that from Fe–Ca sludge. The NH_3 emission curve of Fe–Ca–C sludge was similar to that of RS, and the presence of coal brought about a bigger and broader peak.

For wet sludge, a single peak appeared instead of two peaks because of the temperature delay effect. The NH_3 yields changed with different water contents, showing that the drying process is an important stage for NH_3 emission.

3.3. C-containing species release characteristics

Organics–C is usually transformed into CH_4 , CO, CO_2 and alkane (C_2H_2 , C_2H_4 , C_2H_6 , etc.) in pyrolysis gas products. Since the influence of water on CH_4 , CO and CO_2 is similar to NH_3 , Fig. 3 only lists the curves of dry sludge.

For RS sample, the gas was mainly released below 773 K. The generation of CH_4 occurred at around 473 K due to the cracking of hydrocarbon, simultaneously accompanied by the formation of CO_2 . With increasing temperature, the release of CO began at 873 K and further increased to form a small peak at 1253 K. Meanwhile, the terminal bonds of organics in char cracked and the second CO_2 release process was observed. Until 1373 K, the emission of CO and CO_2 were still proceeding, indicating that some

non-biodegradable organics still remained in char. Similar to NH_3 , the yields of CO, CO_2 and CH_4 yields in RS pyrolysis were lower.

For Fe–Ca and Fenton–Ca sludge, there was a raise on CH_4 emission for the reason of catalytic cracking of tar. CO was also produced more and released earlier than RS. Furthermore, CaO was capable of fixing CO_2 below 773 K. But with temperature increasing, CaCO_3 gradually decomposed and re-released CO_2 . On one hand, the newly generated CaO may have higher catalytic activity. On the other hand, the re-releasing CO_2 may react with char, both attributing to the increase in CO production. However, the second CO_2 peak detected in Fenton–CaO sludge pyrolysis was not only bigger but also earlier than that in Fe–CaO sludge pyrolysis. It is supposed that non-biodegradable organics in Fenton–CaO sludge was easy to decompose after Fenton oxidation.

Coal contained high fixed carbon, thus presenting a large increase in the emissions of CH_4 and CO_2 from Fe–CaO–C sludge pyrolysis. And a CO peak was observed about 1200 K. In this experiment, the interactions between sludge and coal could not be confirmed. However, Folgueras et al. (2010) has demonstrated that FeCl_3 and CaO added to sludge had an effect on the gaseous products from organic matter in coal. Besides, tar decomposition and secondary reaction of volatile may occur during co-pyrolysis (Li et al., 2013, 2014).

3.4. Kinetic parameters of sludge pyrolysis

Sludge pyrolysis reaction is very complex, and the organics thermal degradation is the main reaction during pyrolysis, thus the temperature region 378–800 K was chosen for kinetic comparison of different sludge.

For each organics' decomposition peak, fittings of $\ln\left(\frac{G(\alpha)}{1-\alpha}\right) - \frac{1}{n}$ line were obtained with best n value (see Fig. 4). Table 3 lists the results of correlation kinetic analysis. In Fig. 4, number 1 and 2 inside the parentheses revealed the order of organics' decomposition peaks. All the correlation coefficients R^2 of fitting lines were above 0.995, showing that the n th-order chemical reaction model was suitable to describe the sludge pyrolysis reaction well.

The values of n from different dry and wet sludge were between 1.45 and 4.08. When the specific surface of decomposition changes with the conversion, the reaction orders greater than 1 can be justified, which is equivalent to the case of composite compounds (Font et al., 2005). For dry sludge pyrolysis, RS had the minimum reaction orders 1.45, but orders in three types of dewatered sludge were much greater, about 3.12–3.87. The higher values of n have a correlation with heterogeneous reactions or diffusional effects (Hu et al., 2007). Thus, the catalysis of iron salt and CaO was likely to enhance the complexity of organics reactions. Folgueras et al. (2013) found the similar phenomenon, the reaction orders of sludge conditioned with FeCl_3 and CaO was two more than that of conventional sludge. Similarly, dry dewatered sludge also had

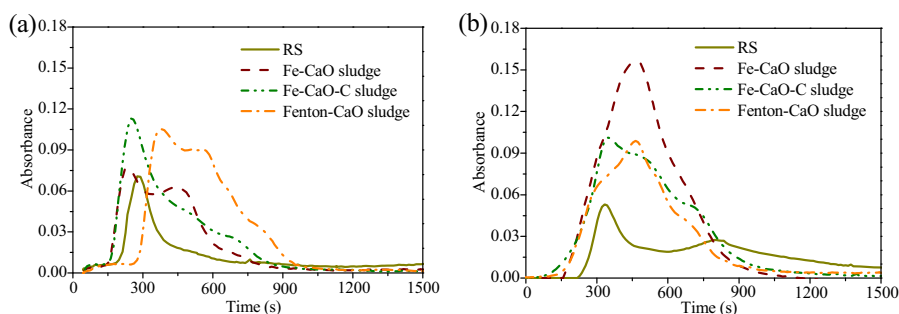


Fig. 2. NH_3 release curves of different sludge: (a) dry sludge and (b) wet sludge.

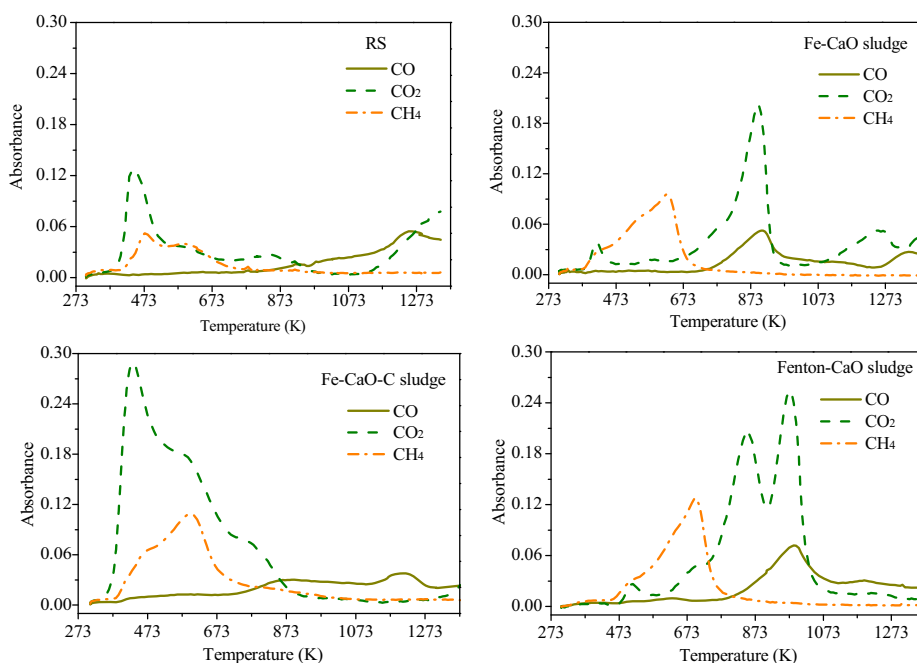


Fig. 3. CH₄, CO₂ and CO release curves of different dry sludge.

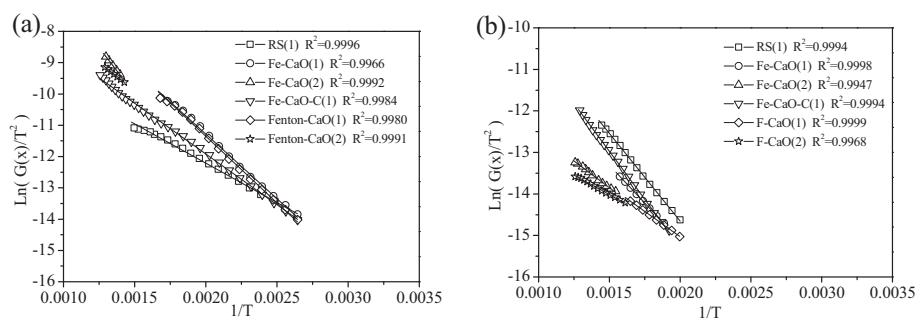


Fig. 4. Kinetic fitting lines of organics decomposition peaks from different sludge: (a) dry sludge and (b) wet sludge.

Table 3

Kinetic parameters of organics decomposition peaks in different sludge pyrolysis.

Materials		First organics peak			Second organics peak		
		<i>n</i>	<i>A</i> /s ^{−1}	<i>E</i> /kJ mol ^{−1}	<i>n</i>	<i>A</i> /s ^{−1}	<i>E</i> /kJ mol ^{−1}
Dry sludge	RS	1.45	0.68	22.02	–	–	–
	Fe–CaO	3.87	31.99	34.27	3.87	208.81	48.95
	Fe–CaO–C	3.12	2.92	26.95	–	–	–
	Fenton–CaO	3.81	38.48	35.32	3.81	7.41	29.87
Wet sludge	RS	2.33	1.36	35.17	–	–	–
	Fe–CaO	4.08	0.26	30.30	1.62	0.03	21.44
	Fe–CaO–C	2.29	1.57	38.37	–	–	–
	Fenton–CaO	2.15	0.03	20.25	1.23	0.01	15.54

higher activation energy and pre-exponential factors. Shao et al. (2010) considered that the addition of CaO and Fe₂O₃ probably increased reaction time of cellulose in sludge. Besides, the CO₂ absorption by CaO also decreases conversion rate at low temperature. On the contrary, the relative stable chemical bonds in coal, providing higher kinetic parameters in Fe–CaO–C sludge pyrolysis.

Wet sludge presented the different performance. The *E* value of wet RS was higher than the dry one. Dry sludge went through smashing before pyrolysis, which brought about a larger reaction surface. In addition, the orders were almost the same except for

Fe–CaO sludge, of which the order was much higher. In contrast, the activation energy of wet Fe–CaO and Fenton–CaO sludge are 30.30 kJ/mol and 20.25 kJ/mol, less than that of wet RS and correlation dry ones. Moreover, all the wet sludge had the lower pre-exponential factors. The differences may be due to water content and physical structure from different sludge. At the initial stage of wet sludge pyrolysis, evaporation of water would consume energy varying with water content. Simultaneously, the temperature difference between internal and external sample will retard the pyrolysis reaction at low temperature. During the direct pyro-

lysis of wet sludge, lumps were formed after drying. It is suggested that partly organics mainly occurs outside the surface of sludge particles, which interfered with the pyrolysis reaction seriously. CaO also acted as skeleton construction during dewatering, therefore the structure of lumps is loose and poriferous. As a consequence, lumps of sludge with more CaO had a better reactivity than RS. Especially, the main reaction of Fe–CaO and Fenton–CaO sludge was the second organic interval, and the higher reaction temperature may provide lower E values.

4. Conclusions

Chemical conditioners had significant influences on sludge pyrolysis characteristics. Coal and CaO/ferric salt may prolong organics reaction time, resulting in more CO, NH₃, CO₂ and CH₄ generation. For wet sludge, pyrolysis reaction was hard to occur completely and the initial degradation of organics occurred at higher temperature. Owing to the dissolution of NH₃/NH₄⁺ in alkaline environment, more NH₃ emitted when wet sludge pyrolysis. Compared with dry raw sludge, dry treated sludge had higher activation energy and pre-exponential factor. Whereas compared with wet raw sludge, wet CaO-conditioned sludge had lower E values, owing to its relative loose structure.

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